RRB-89-36

PCBS AND PESTICIDES IN WATER AT THE MOUTHS OF THE YAMASKA AND SAINT-FRANCOIS RIVERS, QUEBEC IN 1987

by
R.J. Maguire, A. Germain[1],
R.J. Tkacz and S.I. Forrest[1]

Rivers Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, L7R 4A6

May 1989
NWRI Contribution #89-150

[1]Water Quality Branch, Quebec Region, Inland Waters Directorate, Department of Environment, 1001 Rue Pierre Dupuy, Longueuil, Quebec J4K 1A1

ABSTRACT

The analysis of large volume water samples collected over a four week period in 1987 at the mouths of the Yamaska and Saint-François Rivers revealed the presence of PCBs and many pesticides which had not been detected previously in either of these two rivers. Most of the chemicals determined were found in the centrifuged water as opposed to the suspended solids, a phenomenon explained by the low to medium lipophilicity of the chemicals in question. In general, there were more pesticides in the Yamaska River than in the Saint-François River, a finding which was expected since agriculture is more prominent in the basin of the former river. Although the atrazine concentration by far surpassed the levels of the other chemicals determined, it did not exceed the proposed water quality guideline for atrazine of 2 µg/L for the protection of aquatic life.

RÉSUMÉ

L'analyse des échantillons d'eau à grand volume prélevés au cours d'une période de quatre semaines en 1987 à l'embouchure de la rivière Yamaska et de la Saint-François au Québec a revélé la présence de BPC et de quelques pesticides qui n'avaient pas été détectés auparavant dans ces deux rivières. La majorité des produits chimiques détectés l'ont été dans l'eau centrifugée et non dans les sédiments en suspension, ce qui peut être expliqué par la lipophilicité basse à moyenne de ces produits. En général, il y avait plus de pesticides dans la rivière Yamaska que la Saint-François, un résultat prévisible à cause un niveau plus élevé d'activités agricoles dans la Yamaska. La concentration de l'atrazine était plus élevée que celle des autres produits chimiques, par contre elle ne dépassait pas la limite de 2 µg/L proposé dans les lignes directrices pour la protection de la vie aquatique.

MANAGEMENT PERSPECTIVE

The analysis of large volume water samples collected over a four week period in 1987 at the mouths of the Yamaska and Saint-François Rivers revealed the presence of PCBs and many pesticides which had not been detected previously in either of these two rivers. Most of the chemicals determined were found in the centrifuged water as opposed to the suspended solids, a phenomenon explained by the low to medium lipophilicity of the chemicals in question. In general, there were more pesticides in the Yamaska River than in the Saint-François River, a finding which was expected since agriculture is more prominent in the basin of the former river. Although the atrazine concentration by far surpassed the levels of the other chemicals determined, it did not exceed the proposed water quality guideline for atrazine of 2 µg/L for the protection of aquatic life.

PERSPECTIVE DE GESTION

L'analyse des échantillons d'eau à grand volume prélevés au cours d'une période de quatre semaines en 1987 à l'embouchure de la Rivière Yamaska et de la Saint-François au Québec a revélé la présence de BPCs et de quelques pesticides qui n'avaient pas été détectés avant dans ces deux rivières. De tous les produits chimiques détectés dans l'eau centrifugée et dans les sédiments en suspension, la plupart ont été trouvés dans l'eau. Ceci pouvant être expliqué par la lipophilicité basse à moyenne de ces produits. En général, il y avait plus des pesticides dans la Rivière Yamaska que la Saint-François, un résultat attendu dû à un niveau plus élevé d'activités agricoles dans la première. La concentration de l'atrazine était plus élevée que celle des autres produits chimiques, par contre elle ne dépassait pas la limite de 2 µg/L proposé dans les lignes directrices pour la protection de la vie aquatique.

INTRODUCTION

The Yamaska River basin in Quebec is the focus of intensive agricultural activity. In 1982, 26% of all agricultural pesticides (excluding oils) purchased in Quebec were sold in the Yamaska River basin, more than in any other basin (1). The main pesticide classes used in the Yamaska River basin were triazines and triazoles (38% of total, excluding oils), amides (18%), carbamates (16%) and organophosphates (7%). By contrast, in the same year only 4% of all pesticides sold for agricultural purposes in Quebec were bought in the basin of the neighbouring Saint-François River, another major tributary of the Saint Lawrence River (1). The main classes used in the Saint-François River basin were triazines and triazoles (47%), phenoxyacids (13%) and carbamates (9%).

The water quality (C,N,P) of the Yamaska and Saint-François Rivers has been studied extensively (2-4). In addition, there are data on the presence of metals in sediments from various locations in the Yamaska River basin (2). Mongeau (5) documented an average Hg concentration of 0.75 mg/kg wet weight in 17 species of fish taken from various locations in the Yamaska River in 1970-1971.

Occasional surveys for organic contaminants in the Yamaska River have been made over the past twenty years. Duval and Gauthier (6), in the Saint Lawrence River Committee study, reported pesticide concentrations in water at the mouth of the Yamaska River in May-September 1976 in the following ranges: atrazine, 0.1-6.4 µg/L;

de-ethyl atrazine (ADE), 0.1-1.7 µg/L; de-isopropyl atrazine (ADI), <0.02-0.4 µg/L. In July 1980, they found up to 5.4 µg/L atrazine, 1.4 µg/L ADE and 1.0 µg/L ADI near the mouths of the Yamaska and Saint-François Rivers (6). In May-September 1976, concentrations of 2,4-dichlorophenoxyacetic acid (2,4-D) ranged from <0.002 to 0.036 µg/L, while in 1980 its maximum concentration was 0.015 µg/L. Concentrations of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) ranged from not detected (n.d.) to 0.032 µg/L in May-September 1976, compared to <0.002 to 0.006 µg/L in 1980/81. Silvex concentrations did not exceed the limit of detection in any of the 1976 samples, while some residues were found (0.003 µg/L) in 1980 and 1981 (6). In August 1978, concentrations of atrazine in sediment in the Yamaska River and at its mouth were <0.05 mg/kg dry weight.

In 1977-78, average concentrations (wet weight) in the flesh of fish from various reaches of the Yamaska River were <1 mg/kg for total DDT and 0.6 mg/kg for total PCBs (7). In the same samples, hexachlorobenzene, dieldrin, gamma-chlordane, lindane, heptachlor and some heavy metals were also found. The average concentrations of metals and organic contaminants determined in these fish were similar to averages from fish taken from the St. Lawrence River.

In another survey of PCB contamination of fish and mussels in a number of Quebec rivers in 1978 (8), PCBs were found in mussels downstream of Farnham (0.03 mg/kg wet weight) and in fish downstream of Sainte-Hyacinthe (0.8 mg/kg wet weight). Contamination was more pronounced in fish in the Saint-François River, especially downstream

of Sherbrooke (2.0 mg/kg wet weight). A companion survey of organochlorine pesticides in the same year revealed concentrations of total DDT in fish in the range 0.1-0.2 mg/kg wet weight in some fish taken downstream of Sainte-Hyacinthe and upstream of Saint-Pie on the Noire River, a tributary of the Yamaska River (9). As well, total DDT concentrations in fish up to 0.3 mg/kg wet weight were found in the Saint-François River downstream of Magog.

In a similar survey in 1980 (10), PCBs were found in sediment (0.2 mg/kg dry weight), macrophytes (V. americana) (0.4 mg/kg dry weight) and suckers (C. commersoni) (1.1 mg/kg wet weight) downstream of Sainte-Hyacinthe, and in macrophytes (0.5 mg/kg dry weight) downstream of Farnham. Lesser contamination was found in other areas sampled in the Yamaska River basin. PCBs were found in macrophytes (0.2 mg/kg dry weight) in the Saint-François River downstream of Lac Aylmer, Lac Memphremagog and Drummondville. PCBs were also found in fish up to 2.4 mg/kg wet weight at several locations in the Saint-François River. In the same year organochlorine pesticides analyses revealed a concentration of 0.4 mg/kg dry weight for total DDT in macrophytes downstream of Lac Waterloo (11). A muskellunge caught at Waterloo had 1.3 mg/kg wet weight total DDT, and suckers and walleye from various reaches in the river had up to 0.5 mg/kg wet weight. Suckers and pike taken from several locations in the Saint-François River had up to 0.3 mg/kg wet weight total DDT.

In a larger study of the impact of agriculture on the quality of the water in the Yamaska River basin, five sub-basins of the Yamaska

River with almost exclusive agricultural use were examined: the Salvail, a la Barbue, Chibouet, Runnets and Saint-Nazaire Rivers (12,13). Atrazine and N-deethylated atrazine residues ranged in concentration from 0.01 to 26.9 µg/L and <0.01 to 1.34 µg/L, respectively, over April to December 1974 and 1975. The highest levels of atrazine were observed in July each year and were compatible with its time of application and with heavy rains. It was estimated that 0.1-3% of all atrazine applied to each watershed was lost to drainage waters.

In a more recent study, the concentrations of atrazine, diazinon and 2,4-D were found to exceed their respective guidelines for aquatic life (2.0, 0.08 and 4.0 µg/L) in the Yamaska and Saint-François river basins in 1987/88 (14). The concentration of atrazine at the mouth of the Yamaska River ranged from 2.1 to 17.5 µg/L in the period June-October, 1987, and from n.d. to 2.1 µg/L in the period May-June, 1988. Atrazine was also detected at 0.4-2.9 µg/L in the Yamaska South River as well as in the Chibouet and David Rivers (tributaries of the Yamaska River) in May-June, 1988. At the mouth of the Yamaska River, the diazinon concentration ranged from n.d. to 2.2 µg/L in May-June 1988, and from 0.2 to 5.7 µg/L in the Yamaska South River and the two tributaries over the same period. Generally, lower concentrations of atrazine were found in the Saint François River than in the Yamaska River, from 0.2 to 1.6 µg/L in June-October 1987 and from n.d. to 0.3 µg/L in the period May-June 1988. Atrazine was found at concentrations of 0.3 and 0.5 µg/L, respectively, in the Saint-Germain and

Aux Vaches tributaries of the Saint-François River in May 1988. The concentration of 2,4-D ranged from 1.0 to 4.6 µg/L in the Saint-François River mouth in June-August, 1987, but was not detected in the tributaries of that river. The concentrations of PCBs and organochlorine pesticides did not exceed the limits of detection in any samples analyzed in this study (14).

This reports presents the results of a more extensive survey of 116 PCB congeners, organochlorine, organophosphorus, triazine, amide and carbamate pesticides at the mouths of the Yamaska and Saint-François Rivers at four one-week intervals in the summer of 1987.

EXPERIMENTAL SECTION

Materials

Pesticide standards were obtained from chromatographic supply companies. Sets of PCB congeners were obtained from the National Research Council of Canada, Halifax, N.S. These PCB congeners represent, by weight, 3% of Aroclor 1221, 44% of Aroclor 1242, 48% of Aroclor 1248, 38% of Aroclor 1254 and 60% of Aroclor 1260; therefore the sum of the PCB congeners reported in this study should not be regarded as "total PCBs". Pesticide grade dichloromethane and other solvents were obtained from different suppliers and their purity (at 1000x concentration) was checked before use. The sodium sulfate, aluminum foil, glass fibre filters and disposable pipets were heated

to 500°C for 24 h before use. All glassware was rinsed with pesticide grade solvents before use. ACRO LC 13 disposable filters with Luer inlets were obtained from Gelman Sciences (Montreal, Quebec).

Methods

Water and bottom sediment samples were collected at the mouths of the Yamaska (lat. 46°03'02", long. 73°56'45") and Saint-François (lat. 46°06'55", long. 73°54'30") Rivers at four dates in July and August 1987. Two hundred litres of water was passed through a Westphalia centrifuge at a rate of 6 L/min. Following centrifugation, the clarified water was collected and then extracted in a large volume aqueous phase liquid extractor (APLE) (15). The extraction efficiency of the APLE for a number of chlorinated pesticides and hydrocarbons in centrifuged natural waters in the 0.05-1 ng/L range varies from 70 to 123%, with an overall mean recovery of 93% (14).

The suspended solids were analyzed by Novalab Ltd. (9420 Cote de Liesse, Lachine, Quebec HBT 1A1) according to Inland Waters Directorate methods (16). Table 1 shows those chemicals for which determinations were made in suspended solids, and their limits of detection. In contrast to the individual PCB congener determinations performed on the extracts of centrifuged water, PCB analyses of the suspended solids were performed for Aroclors 1242, 1254 and 1260.

The dichloromethane extracts (which contained water) from the APLE were analyzed at the National Water Research Institute. The phases were separated and the dichloromethane was dried and reduced to

10 mL in volume with a rotary evaporator. The solvent was changed to hexane and reduced to 1-2 mL by evaporation with a gentle stream of nitrogen. At this point, there was usually some precipitation in the test tube, but all material was transferred to the clean-up column as described below. The hexane extracts were loaded on 20 cm x 1 cm i.d. columns of activated silica gel with a layer of sodium sulfate for drying, and eluted sequentially with 60 mL each of (i) hexane, (ii) 80% hexane - 20% dichloromethane (v/v), (iii) dichloromethane and (iv) methanol. At each solvent change, a little solvent was used to rinse the test tubes containing the original extract, and in this way even the precipitated material was transferred to the clean-up column. Most of the PCBs and insecticides sought eluted in the first three fractions. The first three fractions were dried, concentrated and solvent-changed to toluene with a final volume of 1.0 mL. Gas chromatographic analyses for PCBs and chlorinated, organophosphate, triazine and amide pesticides were performed on the first three fractions only. High performance liquid chromatographic analyses for carbamate pesticides were performed on all four fractions, after the solvent had been changed to 35% acetonitrile - 65% water, as described below.

PCBs and chlorinated pesticides

Analyses of the sample extracts for PCBs and chlorinated pesticides were performed with a Hewlett-Packard 5890A gas chromatograph

with a single splitless injector-dual column-dual electron capture detector technique. One column was Ultra-2 and the other was OV-17. Column dimensions were 0.2 mm i.d. x 25 m in length, with 0.17 μm film thickness. Injector and detector temperatures were 250 and 350°C, respectively. The initial column temperature was 60°C, and the program rate was 3°/min to 280°C, with an 8 min final hold. The carrier gas flow rate was 1-1.5 mL/min. The identities of the 67 chlorinated insecticides and PCB congeners sought are shown in Table 2. Standard mixtures of all of these compounds in the expected concentration ranges were prepared and used to calibrate retention times and detector responses. Chromatographic "windows" were typically 0.04 min at their widest at 80 min retention time. The presence of a compound was taken to be tentatively confirmed if (i) it occurred within the appropriate chromatographic window on both columns, (ii) the concentrations determined with each column were within 50% of each other (in which case the lower of the two concentrations was reported), and (iii) the concentrations were above the limit of quantitation for the particular sample, as opposed to the limit of detection (17). The limits of quantitation for the 67 compounds sought were typically about 0.01 ng/L for a 200 L sample, about three times the limits of detection.

Organophosphorus, triazine and amide pesticides

Analyses of the sample extracts for organophosphorus, triazine and amide pesticides were performed in splitless mode with a Varian

3400 gas chromatograph and a thermionic specific detector. A 25 m x 0.32 mm i.d. Ultra-2 column (0.17 µm film thickness) was programmed from 80°C to 280°C at 4°/min followed by a 5 min hold. The inlet and detector temperatures were 250 and 280°C, respectively. The carrier gas, nitrogen make-up, air and hydrogen flow rates were 1.0-1.5, 29, 175 and 4.5 mL/min, respectively. The identities of the the 32 organophosphorus, triazine and amide pesticides sought are shown in Table 3. Standard mixtures of all these compounds in the expected concentration ranges were prepared and used to calibrate retention times and detector response. The presence of a compound was taken to be tentatively confirmed if (i) it occurred within the appropriate chromatographic window, and (ii) the concentration was above the limit of quantitation (17). The limits of quantitation for the 32 compounds sought were about 0.01 ng/L for a 200 L sample, about three times the limit of detection.

Carbamate pesticides

Analyses of the sample extracts for carbamate pesticides were performed by high performance liquid chromatography (HPLC). The 1 mL toluene solutions resulting from the four-fraction cleanup were evaporated almost to dryness with a gentle stream of nitrogen at 35°C and 1 mL acetonitrile was added to the test tube. The acetonitrile was likewise evaporated almost to dryness, and the contents of the test tube were reconstituted with 1 mL of 35% acetonitrile - 65% water

preparatory to analysis by high performance liquid chromatography (HPLC). The third and fourth fractions reconstituted this way occasionally were cloudy, and were therefore filtered using ACRO LC13 disposable filters. Analyses were performed with a Waters Associates HPLC (Millipore-Waters, Mississauga, Ontario) and 990+ diode array spectrophotometric detector. Samples of 10-50 µL volume were injected with a Waters WISP 712 autosampler onto a 15 cm x 4.6 mm i.d. reverse-phase Supelcosil LC-8-DB column preceded by a Supelguard LC-8-DB guard column (Supelco, Oakville, Ontario). Both guard and analytical columns were thermostatted at 35°C. The identities of the 17 carbamate pesticides for which determinations were made are shown in Table 4. The optimal detector wavelength was 220 nm, and the optimal gradient conditions are also shown in Table 4. Standard mixtures of all these carbamates were prepared and used to calibrate retention times and detector responses. Chromatographic windows were typically 0.03 min at their widest at 20 min retention time. The presence of a carbamate was taken to be tentatively confirmed if (i) it occurred within the appropriate chromatographic window, and (ii) its concentration was above the limit of quantitation (17). The limits of quantitation were typically 0.1 ng/L for a 200 L sample, about three times the limit of detection.

In addition to the determination of carbamate pesticides, the diode array detector was used to take 200-800 nm spectra of the HPLC effluent every 200 ms in order to check for the presence of disperse dyes which might have eluted under the conditions used for the carbamates, but none was detected.

RESULTS AND DISCUSSION

In contrast to the observations with centrifuged water, very few chemicals were detected in the suspended solids collected at the mouths of the Yamaska and Saint-François Rivers in July and August, 1987. This is not surprising since many of the chemicals sought have log K_{ow} <3-4 and would not be expected to partition appreciably to the suspended solids (18). Aroclor 1254 and atrazine were the only chemicals found in the suspended solids from the Yamaska River (cf. Table 5), while in the Saint-François River suspended solids samples only Aroclor 1254 was detected (cf. Table 6).

Tables 7-10 show concentrations of chemicals found in extracts of the centrifuged water from the mouths of the Yamaska and Saint-François Rivers. Many of these chemicals have never been observed before in these rivers. Low concentrations of PCB congeners and some chlorinated pesticides were observed in both rivers, while contamination by organophosphate, triazine and amide pesticides was generally greater in the Yamaska River than in the Saint-François River. This latter result was expected since pesticide use in the Yamaska River basin is much heavier than in the Saint-François River basin. Atrazine was found consistently in the Yamaska River samples at concentrations approaching 100 times that of any other pesticide. Atrazine was also found at relatively high concentrations in the Saint-François River samples, albeit not as high or as consistently as in the Yamaska River samples. The presence of atrazine was expected since it is used

on corn, a crop which is grown extensively in these areas. At no time did the atrazine concentration in these samples exceed the proposed water quality guideline of 2 µg/L (19) for the protection of aquatic life, in contrast to the results of other workers who found atrazine concentrations to exceed the guidelines in 1987/88 (14). This discrepancy may have been due to normal environmental variation.

The PCB results from the centrifuged water are not directly comparable to those of the suspended solids since in the former case individual congeners were sought, while in the latter case the determinations were done on an Aroclor basis. The only case in which a direct comparison can be made is for atrazine in the Yamaska River on July 22, 1987 when observed concentrations were 40 ng/g dry weight for suspended solids and 1490 ng/L for the centrifuged water. On that date, the concentration of suspended solids in water was 50 mg/L. Thus the calculated concentration of atrazine in bulk uncentrifuged water was 1492 ng/L, and >99% of the atrazine was in the operationally-defined dissolved phase (i.e., in centrifuged water). An apparent suspended solids to water partition coefficient (K_p) of 27 µg/kg/µg/L can be calculated from these data, in substantial agreement with the value of 18 calculated using the equation (18)

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346$$

where K_{ow} is the octanol-water partition coefficient (4.27×10^2, ref. 20) and K_{oc} is the organic carbon normalized partition coefficient, equal to K_p divided by the fractional organic carbon content of suspended solids (usually assumed to be 0.1).

ACKNOWLEDGEMENTS

We thank G.J. Pacepavicius and S.P. Batchelor for help with the analyses.

REFERENCES

1. Reiss, R., Perron, F., Paré, J. and St.-Jean, R. Les pesticides en agriculture au Québec en 1982. Environment Canada - Ministère de l'Environnement du Québec Report, Québec, Québec ISBN 0-662-92576-9, 134+ pp., May 1984.
2. Bélanger, B. Rapport annuel 1979 de la qualité de l'eau des lacs et des rivières du bassin Yamaska. Rapport No. 80-16, Environnement Quebec, Service de la qualité des eaux, Sainte-Foy, Québec, March 1980, 58+ pp.
3. Campbell, P.G.C., Cluis, D. and Couture, P. Transformation de la qualite d'une même eau de rivière lors de son séjour dans deux réservoirs differents: (A) le lac Boivin et (B) la réserve de Granby, Québec, Canada. Can. Water Resources J. 7, 127-150 (1982).

4. Campbell, P.G., Couture, P., Lachance, M. and Talbot, L. Étude integrée de la qualité des eaux des bassins versants des rivières Saint-Francois et Yamaska. Vol. 2: Secteur des substances nutritives. Rapport Q.E. 17, Ministère des richesses naturelles, Direction générale des eaux, Sainte-Foy, Québec, Sept. 1976, 127+ pp.

5. Mongeau, J.-R. Les poissons du bassin du drainage de la rivière Yamaska, 1963 à 1975. Rapport Technique, Ministère du tourisme, de la chasse et de la peche, Service de l'aménagement et de l'exploitation de la faune, Montréal, Québec, June 1979, 191+ pp.

6. Duval, D. and Gauthier, R. Présence des herbicides dans le fleuve Saint-Laurent et ses tributaires. Water Quality Program Report, Inland Waters Directorate, Dept. of Environment, Longueuil, Quebec, 1986, 30+ pp.

7. Harvey, G. Les metaux lourds et les composés organochlorés dans la chair des poissons du bassin versant de la Yamaska. Rapport Technique No. 06-30, Ministère du loisir, de la chasse et de la peche, Service de l'aménagement et de l'exploitation de la faune, Québec, Québec, ISBN 2-550-00628-3, 89+ pp., Nov. 1979.

8. Goulet, M. and Laliberté, D. BPC: contamination du milieu aquatique au Québec méridional. Réseau de surveillance des substances toxiques dans le milieu aquatique. Rapport No. Q.E.-53, Ministère de l'environnement du Québec, Service de la qualité des eaux, Sainte-Foy, Québec, Dec. 1982, 44+ pp., ISBN 2-550-10146-4.

9. Laliberté, D. and Goulet, M. Pesticides organochlorés. Contamination du milieu aquatique au Québec méridional. Réseau de surveillance des substances toxiques dans le milieu aquatique. Rapport No. Q.E.-54, Dec. 1983, Ministère de l'environnement du Québec, Service de la qualite des eaux, direction générale des inventaires et de la recherche, Québec, Québec, 70+ pp.

10. Croteau, G., Goulet, M. and Laliberté, D. Biphényles polychlorés: contamination du milieu aquatique au Québec méridional en 1980. Réseau de surveillance des substances toxiques dans le milieu aquatique. Rapport No. 84-17, Ministère de l'environnement, service de la qualité des eaux, direction générale des inventaires et de la recherche, Québec, Oct. 1984, 75+ pp.

11. Paul, M., Laliberté, D. and Goulet, M. Réseau de surveillance des substances toxiques 1980: pesticides organochlorés dans le milieu aquatique au Québec méridional. Rapport No. 84-20, Environnement Québec, Direction générale des ressources hydriques, direction des relevés aquatique, Québec, Oct. 1984, 59+ pp.

12. Caillé, A., Campbell, P.G., Cluis, D., Couture, P. and Talbot, L. Impact de l'agriculture sur la qualité des eaux de surface du bassin de la rivière Yamaska. INRS-Eau Rapport Scientifique No. 50, Université du Québec, C.P. 7500, Sainte-Foy, Québec, 1975.

13. Muir, D.C.G., Yoo, J.Y. and Baker, B.E. Residues of atrazine and N-deethylated atrazine in water from five agricultural watersheds in Quebec. Arch. Environ. Contam. Toxicol. 7, 221-235 (1978).

14. Forrest, S.I. and Caux, P.-Y. Pesticides in tributaries of the St. Lawrence River (including certain C.E.P.A. priority list contaminants), 1987-1988 Program Report, Centre Saint-Laurent, Hydrology and Networks, Environment Canada, Longueuil, Québec J4K 1A1 (1989).

15. McCrea, R.C. and Fischer, J.D. Design and testing of an aqueous phase liquid-liquid extractor (APLE) for the determination of organochlorine contaminants. Inland Waters Directorate Technical Bulletin No. 138, Water Quality Branch - Ontario Region, Department of Environment, Canada Centre for Inland Waters, Burlington, Ontario, Canada L7R 4A6, ISBN 0-662-14341-8, 11+ pp., 1985.

16. Inland Waters Directorate. Analytical Methods Manual Update, 1981. Water Quality Branch, Inland Waters Directorate, Department of Environment, Ottawa, Ontario, Canada K1A 0E7 1981.

17. Keith, L.H., Crummett, W., Deegan, W., Libby, R.A., Taylor, J.K. and Wentler, G. Principles of environmental analysis. Anal. Chem. 55, 2210-2218 (1983).

18. Karickhoff, S.W. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10, 833-846 (1981).

19. Department of Environment. Draft Canadian Water Quality Guidelines: Atrazine. Water Quality Branch, Inland Waters Directorate, Department of Environment, Hull, Quebec K1A 0E7, 22+ pp., March 1989.

20. Veith, G.D., DeFoe, D.L. and Bergstedt, B.V. Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish. Res. Board Can. 36, 1040-1048 (1979).

21. Ballschmiter, K. and Zell, M. Analysis of polychlorinated biphenyls by capillary gas chromatography. Fresenius Z. Anal. Chem. 302, 20-31 (1980).

Table 1. Chemicals sought in suspended solids.*

Chemical	Limit of Detection, ng/g
hexachlorobenzene	5
heptachlor	5
aldrin	5
p,p'-DDE	5
mirex	5
α-BHC	5
lindane	5
β-BHC	5
heptachlor epoxide	5
cis-chlordane	10
trans-chlordane	10
p,p'-DDD	5
p,p'-DDT	5
o,p'-DDD	5
o,p'-DDT	5
methoxychlor	10
α-endosulfan	5
dieldrin	5
endrin	10
β-endosulfan	5
Aroclor 1242	5
Aroclor 1254	5
Aroclor 1260	5
aldicarb	2000
butylate	200
carbofuran	200
dicamba	50
2,4-dichlorophenoxyacetic acid	100
2-(2,4-dichlorophenoxy)propionic acid	50
2-(2,4-dichlorophenoxy)butyric acid	50
2,4,5-trichlorophenoxyacetic acid	50
silvex	50
alachlor	400
metolachlor	200
atrazine	10
metribuzin	20
diazinon	20
methyl parathion	20
malathion	20
fenitrothion	20
parathion	20

*Limits of detection are given for a 10 g sample on a dry weight basis.

Table 2. Chlorinated hydrocarbons sought in centrifuged water.[1]

No.	Abbreviation	Name
1	lindane	γ-hexachlorocyclohexane
2*	PCB 18	2,2',5-trichlorobiphenyl
3*	PCB 15	4,4'-dichlorobiphenyl
4*	PCB 54	2,2',6,6'-tetrachlorobiphenyl
5*	PCB 31	2,4',5-trichlorobiphenyl
6	heptachlor	heptachlor
7	PCB 52	2,2',5,5'-tetrachlorobiphenyl
8*	PCB 49	2,2',4,5'-tetrachlorobiphenyl
9	aldrin	aldrin
10	PCB 44	2,2',3,5'-tetrachlorobiphenyl
11*	PCB 40	2,2',3,3'-tetrachlorobiphenyl
12*	PCB 103	2,2',4,5',6-pentachlorobiphenyl
13	heptachlor epoxide	heptachlor epoxide
14*	PCB 121	2,3',4,5',6-pentachlorobiphenyl
15*	PCB 60	2,3',4,4'-tetrachlorobiphenyl
16*	o,p'-DDE	o,p'-DDE
17*	PCB 101	2,2',4,5,5'-pentachlorobiphenyl
18*	α-endosulfan	α-endosulfan
19*	PCB 86	2,2',3,4,5-pentachlorobiphenyl
20*	PCB 87	2,2',3,4,5'-pentachlorobiphenyl
21	dieldrin	dieldrin
22*	p,p'-DDE	p,p'-DDE
23*	PCB 77	3,3',4,4'-tetrachlorobiphenyl
24*	PCB 154	2,2',4,4',5,6'-hexachlorobiphenyl
25*	o,p'-TDE	o,p'-TDE
26	endrin	endrin
27*	PCB 51	2,2',3,5,5',6-hexachlorobiphenyl
28*	β-endosulfan	β-endosulfan
29*	PCB 118	2,3',4,4',5-pentachlorobiphenyl
30*	PCB 143	2,2'3,4,5,6'-hexachlorobiphenyl
31*	p,p'-TDE	p,p'-TDE
32*	PCB 114	2,3,4,4',5-pentachlorobiphenyl
33	o,p'-DDT	o,p'-DDT
34*	PCB 153	2,2',4,4',5,5'-hexachlorobiphenyl
35*	PCB 105	2,3,3',4,4'-pentachlorobiphenyl
36	PCB 141	2,2',3,4,5,5'-hexachlorobiphenyl
37*	PCB 137	2,2',3,4,4',5-hexachlorobiphenyl
38	p,p'-DDT	p,p'-DDT
39*	PCB 138	2,2',3,4,4',5'-hexachlorobiphenyl
40*	PCB 129	2,2',3,3',4,5-hexachlorobiphenyl
41	PCB 159	2,3,3',4,5,5'-hexachlorobiphenyl
42	PCB 182	2,2',3,4,4',5,6'-heptachlorobiphenyl
43	PCB 187	2,2',3,4',5,5',6-heptachlorobiphenyl
44	PCB 183	2,2',3,4,4',5',6-heptachlorobiphenyl
45*	PCB 128	2,2',3,3',4,4'-hexachlorobiphenyl

cont'd next page

Table 2. cont'd

No.	Abbreviation	Name
46*	PCB 185	2,2',3,4,5,5',6-heptachlorobiphenyl
47*	PCB 202	2,2',3,3',5,5',6,6'-octachlorobiphenyl
48*	PCB 171	2,2',3,3',4,4',6'-heptachlorobiphenyl
49*	PCB 156	2,3,3',4,4',5-hexachlorobiphenyl
50*	PCB 173	2,2',3,3',4,5,6-heptachlorobiphenyl
51*	PCB 200	2,2',3,3',4,5',6,6'-octachlorobiphenyl
52*	methoxychlor	methoxychlor
53*	PCB 180	2,2',3,4,4',5,5'-heptachlorobiphenyl
54*	PCB 191	2,3,3',4,4',5',6-heptachlorobiphenyl
55*	mirex	mirex
56	PCB 170	2,2'3,3',4,4',5-heptachlorobiphenyl
57	PCB 201	2,2',3,3',4',5,5',6-octachlorobiphenyl
58	PCB 203	2,2',3,4,4',5,5',6-octachlorobiphenyl
59*	PCB 196	2,2',3,3',4,4',5',6-octachlorobiphenyl
60*	PCB 189	2,3,3',4,4',5,5'-heptachlorobiphenyl
61*	PCB 208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl
62*	PCB 195	2,2',3,3',4,4',5,6-octachlorobiphenyl
63*	PCB 207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl
64	PCB 194	2,2',3,3',4,4',5,5'-octachlorobiphenyl
65	PCB 205	2,3,3',4,4',5,5',6-octachlorobiphenyl
66*	PCB 206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
67*	PCB 209	decachlorobiphenyl

[1]Chemicals are listed in order of elution from an Ultra-2 column. The IUPAC number scheme for the PCB congeners is given in ref. 21.

*Not present above limit of quantitation in any sample.

Table 3. Organophosphate, triazine and amide pesticides sought in centrifuged water.*

oxydemeton-methyl
dichlorvos
acephate
mevinphos
trichlorfon
demeton-S
deethylated atrazine
naled
phorate
sulfotepp
dimethoate
demeton-O
atrazine
terbufos
alachlor
diazinon
disulfoton
metribuzin
prometryn
malathion
fenthion
chlorpyrifos
parathion
cyanazine
anilazine
methidathion
crotoxyphos
fensulfothion
ethion
phosmet
azinphos-methyl
phosalone

*Pesticides are listed in order of elution from an Ultra-2 column.

Table 4. Carbamate pesticides sought in centrifuged water.*

aldicarb sulfoxide
aldicarb sulfone
methomyl
phenmedipham
desmedipham
thiram
aldicarb
thiophanate-methyl
propoxur
carbofuran
benomyl
carbaryl
pirimicarb
chloropropham
EPTC
cycloate
butylate

*Compounds are listed in order of elution from a Supelcosil LC-8-DB HPLC column under the following conditions, with flow 1 mL/min and linear gradients throughout:

time, min	% acetonitrile	% water
0	35	65
4	48	52
7	51	49
9	55	45
13	100	0
20	100	0
25	35	65

Table 5. Concentrations (ng/g dry weight) of chemicals found in the suspended solids at the mouth of the Yamaska River in 1987.

Chemical	July 16	July 22	July 29	August 4
Aroclor 1254	50	20	20	20
atrazine		40		

Table 6. Concentrations (ng/g dry weight) of Aroclor 1254 found in suspended solids at the mouth of the Saint-François River in 1987.

July 17	July 23	July 28	August 5
60	60	60	40

Table 7. Concentrations (ng/L) of chlorinated pesticides and PCBs in centrifuged water at the mouth of the Yamaska River in 1987.*

Chemical	July 16	July 22	July 29	August 4	August 6
lindane	1.38	0.96	0.80	0.88	1.04
heptachlor				0.03	
PCB 52	0.08			0.05	0.04
heptachlor epoxide	0.05		0.01		0.02
endrin	0.30	0.14	0.07		
o,p'-DDT	0.02	0.02			
p,p'-DDT	0.05				
PCB 187	0.01	0.01	0.01	0.01	
PCB 183		0.01	0.01		
PCB 170	0.01				
PCB 201		0.04			
PCB 203		0.01	0.01		0.04
PCB 194			0.01		
Sum of PCB congeners	0.10	0.07	0.04	0.06	0.08

*Aldrin, dieldrin and PCBs 44, 141, 159, 182 and 205 were not found above their limits of quantitation, in addition to those compounds designated with an asterisk in Table 2.

Table 8. Concentrations (ng/L) of chlorinated pesticides and PCBs in centrifuged water at the mouth of the Saint-François River in 1987.*

Chemical	July 17	July 23	July 28	August 5	August 6
lindane			0.58	0.51	0.18
heptachlor			0.60	0.45	0.92
PCB 52				0.08	
aldrin					0.09
PCB 44			0.16	0.06	0.15
heptachlor epoxide				0.01	0.01
dieldrin	0.01				0.10
endrin					0.07
o,p'-DDT				0.18	
PCB 141			0.02		
p,p'-DDT				0.21	0.48
PCB 159			0.01		
PCB 182			0.01		
PCB 187			0.01	0.01	0.01
PCB 170					0.01
PCB 201					0.01
PCB 205					0.01
Sum of PCB congeners			0.21	0.15	0.19

*PCBs 203 and 194 were not found above their limits of quantitation, as well as those compounds marked with an asterisk in Table 2.

Table 9. Concentrations (ng/L) of organophosphorus, triazine and amide pesticides in centrifuged water at the mouth of the Yamaska River in 1987.*

Pesticide	July 16	July 22	July 29	August 4	August 6
oxydemeton-methyl	2.6	11	5.0	6.8	16
dichlorvos	0.41	0.55	0.65	0.61	0.73
acephate	0.35				0.95
mevinphos	0.36				
trichlorfon	0.94	2.2		0.82	7.3
demeton-S	1.4	0.78	0.66	2.1	1.13
naled		19	14	3.8	
sulfotepp		0.50	0.14	0.35	
dimethoate		0.50	6.92	1.3	0.45
demeton-O		3.3			
atrazine	240	1500	190	890	230
terbufos	0.55	0.10	0.08		
diazinon	0.18	0.10			
disulfoton	1.7	0.38			0.62
prometryn	0.87	1.5		5.3	7.8
malathion	0.20				
fenthion	1.3	0.33	0.22		
chlorpyrifos	0.86	0.13	0.09		
parathion	0.54				
cyanazine		0.47	1.6	0.86	
anilazine		0.34	0.09	0.19	0.34
methidathion		0.62	0.48	1.4	0.56
crotoxyphos			0.97		
ethion		0.15		0.10	
phosalone		10.18		0.55	

*Pesticides are listed in order of elution from an Ultra-2 column. Deethylated atrazine, azinphos-methyl, phorate, alachlor, metribuzin, fensulfothion and phosmet were not found above their limits of quantitation.

Table 10. Concentrations (ng/L) of organophosphorus, triazine and amide pesticides in centrifuged water at the mouth of the Saint-François River in 1987.*

Pesticide	July 17	July 23	July 28	August 4	August 5
oxydemeton-methyl	12				
dichlorvos	0.21	0.06		0.10	0.18
trichlorfon					1.75
demeton-S	0.17		5.1	1.5	1.00
naled			1.8		
sulfotepp	0.12				0.06
dimethoate					0.14
atrazine	133		0.28	0.44	15
terbufos			0.02		
metribuzin	5.2				1.4
prometryn	0.39				
malathion	0.46	0.51	0.46		
chlorpyrifos			0.33	0.23	
cyanazine				0.83	0.75
anilazine					0.05
methidathion		0.41	0.33	1.0	0.28
crotoxyphos					56
ethion			0.07		
phosalone	0.69				

*Pesticides are listed in order of elution from an Ultra-2 column. Acephate, mevinphos, deethylated atrazine, phorate, demeton-O, alachlor, diazinon, disulfoton, parathion, fensulfothion, phosmet and azinphosmethyl were not found above their limits of quantitation.